Study of defect types and room-temperature ferromagnetism in undoped rutile TiO_2 single crystals*

LI Dong-Xiang(李东翔) [a,b], QIN Xiu-Bo(秦秀波)[c], ZHENG Li-Rong(郑黎荣)[d], LI Yu-Xiao(李玉晓)[b], CAO Xing-Zhong (曹兴忠)[a], LI Zhuo-Xin(李卓昕)[a], YANG Jing(杨静) [a], WANG Bao-Yi(王宝义)[a]†

a) Key Laboratory of Nuclear Analysis Techniques, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China
b) School of Physical Engineering, Zhengzhou University, Zhengzhou, 450001, China
c) Research Center for Application of Nuclear Technology, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100049, China
d) Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

(Received X XX XXXX; revised manuscript received X XX XXXX)

Room-temperature ferromagnetism has been experimentally observed in annealed rutile TiO_2 single crystals when magnetic field is applied parallel to the sample plane. By combining X-ray absorption near edge structure spectrum and positron annihilation lifetime spectroscopy, Ti^{3+}-V_O defect complexes (or clusters) have been identified in annealed crystals at high vacuum. We elucidate that the unpaired 3d electrons in Ti^{3+} ions provide the observed room-temperature ferromagnetism. Besides, excess oxygen ions in TiO_2 lattice could induce a number of Ti vacancies which increase magnetic moments obviously.

Keywords: annealing**,** oxygen vacancies, Ti^{3+}-V_O defect complexes, ferromagnetism
PACS: 75.50.Pp, 71.55.-I, 75.20.Hr

1. Introduction

Dilute magnetic semiconductors (DMSs) with magnetic and semiconducting properties are regarded as a new generation material due to their potential applications in spintronic devices.[1,2,3,4,5] Since the first discovery of room-temperature ferromagnetism (RTFM) in Co-doped anatase TiO_2 thin films,[6] several studies have been performed on the magnetism of TiO_2 doped with transitional metal (TM), such

* Project supported by the Young Scientists Fund of the National Natural Science Foundation of China (Grant No. 61006066) and the National Natural Science Foundation of China (Grant No. 11175191).

† Corresponding author. E-mail: wangboy@ihep.ac.cn

as Mn, V, Cr, Nb, Fe and Ni. Different research groups[7,8,9,10] learned about magnetic properties of TM-doped TiO_2 samples using first principles method. But the origin of ferromagnetism in magnetic-transition-element-doped oxide semiconductors is still under debate as to whether ferromagnetism is intrinsic[11,12] or whether it comes from the precipitation of magnetic clusters.[13] Recently, Coey's group[14] reported about magnetism observed in HfO_2 thin films on sapphire or silicon substrates. Hong et al.[15] and Yoon et al.[16] reported room-temperature ferromagnetism in pure TiO_2 films. These are surprising results and have generated a lot of interest in this new phenomenon, also known as d^0 magnetism.[17] Its appearance can exclude the influence of magnetic elements (imported by doping transitional metal) from origin of ferromagnetism.

First principle calculation indicated that the ferromagnetism of undoped rutile TiO_2 largely originates from the d orbitals of low-charge-state Ti ions converted from Ti^{4+} ions induced by the surface oxygen vacancies.[18] But there is little experimental work about origin of room-temperature ferromagnetism in undoped TiO_2 single crystals. In this study**,** the influence of annealing temperature in high vacuum on structure and magnetism has been observed. We try to answer two questions: (i) what is defect types of undoped TiO_2 single crystals annealed in high vacuum. (ii) What is the origin of room-temperature ferromagnetism after high-temperature anneal.

2. Experiments

Commercial rutile TiO_2 single crystals were obtained from institute of Shanghai optics and fine mechanics, Chinese academy of sciences. The size of the samples was $5 \times 5 \times 0.5$ mm^3, corresponding to a mass of 53.25 mg. Some samples were annealed in vacuum annealing furnace (vacuum: 10^{-4}-10^{-5} Pa) from 1023 K to 1273 K for 1 h. The structure and magnetism of TiO_2 single crystals were characterized by x-ray diffraction (XRD), X-ray absorption near edge structure (XANES) spectrum and superconducting quantum interference device (Quantum Design MPMS-XL5) at room temperature. The XANES analyses were performed on the beam lines 1W1B of the Beijing Synchrotron Radiation Facility (BSRF). Positron annihilation lifetime

spectroscopy (PALS) was used to probe the vacancy-type defects of TiO_2 single crystals with ^{22}Na as positron source. Two of the same samples were tightly clamped on both sides of ^{22}Na radioactive sources, forming a sandwich structure. The prompt time resolution of the system was 190 ps. Each spectrum contains total counts of 2×10^6. The lifetime spectra were de-convoluted using the code LT 9.0 software.

3. Results and discussion

The annealed samples in high vacuum changed from transparent to dark-blue, which most possibly relates to F^+ centers (the electrons in singly occupied oxygen vacancies).[19] XRD patterns of virgin and annealed TiO_2 single crystals can be indexed to pure rutile phase. And no impurity phases are detected within the detection limit of instrument. A representative XRD spectrum with annealed TiO_2 single crystal in high vacuum at 1273 K is shown in Fig. 1.

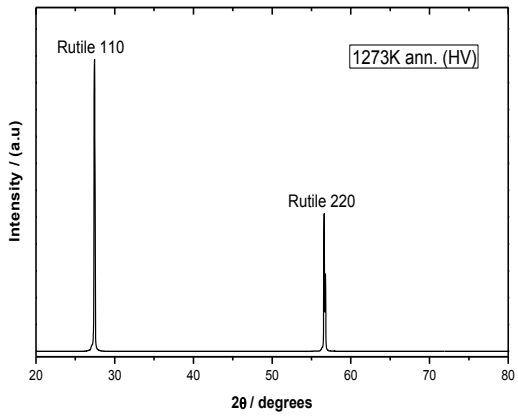

Fig. 1. XRD spectrum of the TiO_2 single crystal annealed in high vacuum at 1273 K.

The pre-edge peaks of the XANES spectra of annealed samples in high vacuum contain three major features denoted as A1, A2, and A3, as are shown in Fig. 2(a). The three protrusions near 4970 eV are related to the 3d electrons of Ti.[20] The origin of the A2 and A3 features are attributed to 1s→3d transitions and assigned to 1s→$2t_{2g}$ and 1s→$3e_g$ transitions in an octahedral field, respectively.[21] The origin of the A1 peak is less clear, but it is also believed to be associated with Ti 3d-4p hybridized states.[21] The Ti pre-edge XANES signals allow us to obtain complementary information on the character of the Ti-O bonding by studying the variation of the

pre-edge peaks.

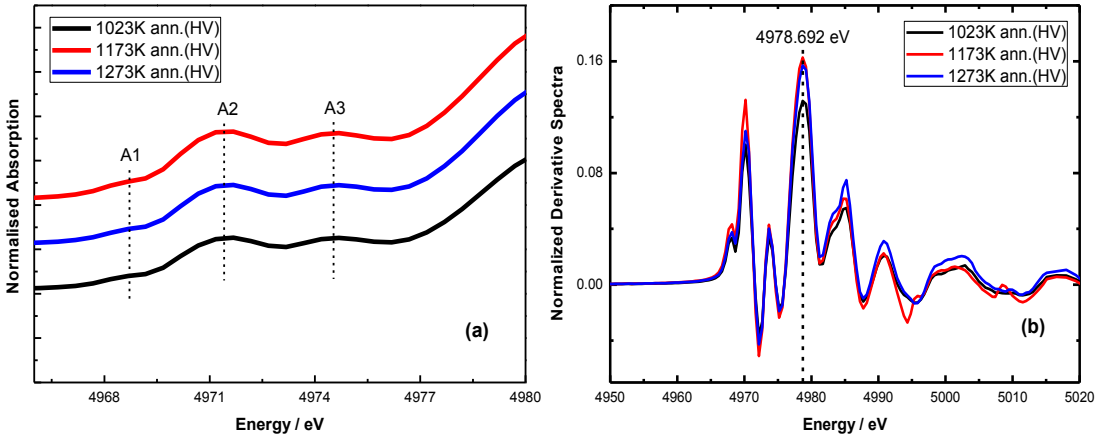

Fig. 2. (Color online) Normalized XANES spectra at the Ti K-edge for annealed TiO_2 single crystals in high vacuum: (a) pre-edge peak spectra. All spectra are plotted on the same vertical scale and displaced vertically for clarity. (b) Normalized derivative spectra.

Normalized derivative spectra of annealed samples in high vacuum are shown in Figure 2(b). Dashed line gives the highest peak corresponding to the energy value. We obtained a value of 4978.692 eV (E_0) for the annealed TiO_2 single crystals in high vacuum. This value is between Ti^{4+} absorption edge at 4979.8 eV and $Ti^{3.4+}$ absorption edge at 4977.2 eV.[22] The presence of a Ti^{3+} species is very likely after high temperature anneal. It is possibly associated with oxygen vacancies according to the following:

$$4Ti^{4+} + O^{2-} \rightarrow 4Ti^{4+} + 2e^{-} + V + 0.5O_2 \rightarrow 2Ti^{4+} + 2Ti^{3+} + V + 0.5O_2,$$

Where V represents an empty position (anion-vacant site) originating from the removal of O^{2-} from the lattice, here represented as an oxygen ion vacancy.

Table 1. LT9.0 fitting results of positron lifetime spectra about annealed samples

Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	I_1 (%)	I_2 (%)	I_3 (%)
1023K ann.	0.1560	0.377	1.854	86.65	9.88	3.47
1073K ann.	0.1572	0.390	1.920	88.98	7.88	3.14
1173K ann.	0.1568	0.400	1.915	89.46	7.57	2.96
1273K ann.	0.1507	0.309	1.807	86.70	10.4	2.92

Fitting results of positron lifetime spectra for annealed samples in high vacuum

are shown in Table 1. The positron annihilation lifetime spectroscopy of TiO_2 single crystals yielded three distinct lifetime components: τ_1, τ_2, and τ_3, with relative intensities I_1, I_2, and I_3. The value of τ_2 is as a major concern on reflecting size and types of defects (vacancies and/or complexes). And its relative intensity (I_2) gives more information on the distribution of these defects. It is well known that defects of efficient positron trap primarily include titanium vacancies, negatively charged and neutral vacancy-type defects in annealed TiO_2 single crystals. In addition, He et al.[23] and Nowotny et al.[24] had clarified that the annealed samples in vacuum existed a good deal of oxygen vacancies and few titanium vacancies. Titanium vacancies were not sensitive to positrons because of low densities. Then combining with test results of XANES and XRD could indicate that changes of τ_2 and I_2 are related to Ti^{3+}-V_O defect complexes. With increase of the annealing temperature from 1023 K to 1173 K, τ_2 increases and I_2 accordingly decreases owing to the generation of more Ti^{3+}-V_O defect complexes and forming of defect clusters, respectively. However, τ_2 decreases and I_2 accordingly increases when annealing temperature rises to 1273 K, indicating that the aggregated defect clusters decompose into smaller defects. It is also shown that aggregated defect clusters in small depth move to the surface.

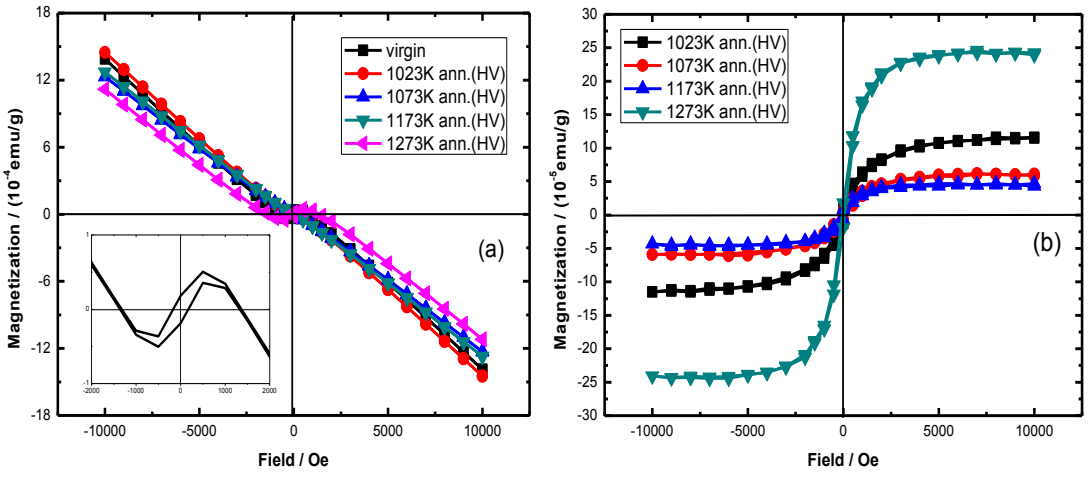

Fig. 3. (Color online) (a) Original ***M***–***H*** curves of virgin and annealed TiO_2 single crystals at 300 K, the latter are annealed from 1023 K to 1273 K in high vacuum. Inset: the low-field part of the loop for 1273 K ann. (HV). (b) ***M***–***H*** loop after deducting the substrate signal.

Fig. 3(a) shows the measured magnetic moments of TiO_2 single crystals at 300 K

before and after annealing from 1023 K to 1273 K in high vacuum. All substrates display diamagnetic behavior[25] that is different from that of Zhou et al. (paramagnetic).[26] The inset shows the low-field part in an enlarged scale of 1273 K annealed sample. The diamagnetism and ferromagnetism are proportional to magnetic field. Fig. 3(b) shows the annealing-fluence-dependent magnetization of TiO_2 single crystals after subtracting diamagnetic background. The saturated magnetization first decreases gradually with increasing annealing temperature, but for the fluence at 1273 K it increases dramatically. We still measured the hysteresis loops at 300 K, demonstrating their room-temperature ferromagnetism. When O is removed, the excess electrons are unpaired.[27] They can occupy the nearby localized Ti 3d orbit and therefore convert Ti^{4+} ions to Ti^{3+} ions. The unpaired 3d electrons in Ti^{3+} ions provide vast spin magnetic moments which are decisively related with the observed ferromagnetism. The change of saturated magnetization possibly depends on aggregation and decomposition of Ti^{3+}-V_O defect complexes (or cluster) by results of XRD, XANES and PALS. With increasing annealing temperature, Ti^{3+}-V_O defect complexes gradually form clusters. Then these clusters decompose into smaller defects at 1273K. Change of defect size is very consistent with shifty trend of saturation magnetization.

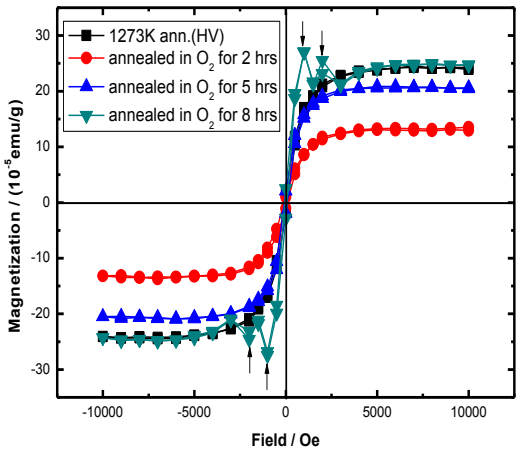

Fig. 4. (Color online) Magnetization versus magnetic field taken at 300 K for TiO_2 single crystals, annealed in O_2 at 1173 K for 2h, 5h and 8h. The anomalous protrusions in the curve are described by arrows. (Note that the signals of substrates were subtracted already.)

In order to check if the magnetism in annealed samples at high vacuum is due to

defects and/or oxygen vacancies, oxygen-annealing tests were done. Data of the oxygen annealed TiO_2 single crystals at 1173 K are shown in Fig. 4 along with the data of 1273 K annealed sample (HV) in order to be able to compare directly. One can clearly see that annealing in oxygen atmosphere for 2 h can reduce the magnetic moments of 1273 K annealed sample (HV) enormously. However, when we increase the duration of annealing up to 5-8 h, saturation magnetization slowly increases. Finally it is basically the same to 1273 K annealed sample (HV). Besides, we observed obvious hysteresis loops and change of color from dark-blue to transparent.

When the sample was second annealing under oxygen condition, oxygen exists as ions in TiO_2 lattice. Therefore, Ti ions must provide corresponding electrons in order to maintain electrostatic balance, which makes Ti ions valence change. Ti ions valence may change from Ti^{3+} to Ti^{4+} when annealing time is 2 h. Saturation magnetization decreases with unpaired 3d electrons reducing. After annealing time increases to 5 h and 8 h, excess oxygen ions in TiO_2 lattice could induce a number of Ti vacancies that make saturation magnetization become large gradually. This evidence has clearly proved that the magnetism of annealed TiO_2 single crystals in high vacuum really originates from oxygen vacancies: filling up vacancies could make unpaired 3d electrons in TiO_2 lattice become lesser, and could make saturation magnetization become weaker.

4. Conclusion

In summary, we have studied local atomic and electronic structures, defect types and magnetism in annealed rutile TiO_2 single crystals by using XRD, XANES, PALS and SQUID. The following conclusion can be determined. (i) A lot of oxygen vacancies and especially Ti^{3+}-V_O defect complexes (or clusters) are formed in high vacuum annealing samples. (ii) Second annealing in oxygen atmosphere can further demonstrate that room-temperature ferromagnetism of annealed samples in high vacuum is closely associated with oxygen vacancies. The unpaired 3d electrons in Ti^{3+} ions provide vast spin magnetic moments which are decisively related to the observed ferromagnetism. Besides, excess oxygen ions in TiO_2 lattice also could induce a

number of Ti vacancies which increase magnetic moments obviously.

References

[1] Dietl T, Ohno H, Matsukura F, Cibert J and Ferrand D 2000 Science **287** 1019

[2] Pearton S J, Heo W H, Ivill M, Norton D P and Steiner T 2004 Semicond. Sci. Technol. **19** R59

[3] Li T J, LI G P, Gao X X and Chen J S 2010 CHIN. PHYS. LETT. **27** 087501

[4] Ouyang Q Z, Ye Z Q, Lei M S, Ouyang C Y, Xiong Z H and Liu G D 2006 Chinese Physics B **15** 1585

[5] Zhao Y H, Cheng L Z, He K Y, Zhao H H, Rong C B and Xu M 2002 Chinese Physics B **11** 77

[6] Matsumoto Y, Murakami M, Shono T, Hasegawa T, Fukumura T, Kawasaki M, Ahmet P, Chikyow T, Koshihara S Y and Koinuma H 2001 Science **29** 854

[7] Xu X G, Jiang Y, Yu G H, Liu Q L and Geng W T 2008 Physics Letters A **372** 2098

[8] Janisch R and Spaldin N A 2006 Phys. Rev. B **73** 035201

[9] Mallia G and Harrison N M 2007 Phys. Rev. B **75** 165201

[10] Du X S, Li Q X, Su H B, and Yang J L 2006 Phys. Rev. B **74**, 233201

[11] Griffin K A, Varela M, Pennycook S J, Pakhomov A B and Krishnan K M 2006 J. Appl. Phys. **99** 08M114

[12] Bryan J D, Santangelo S A, Keveren S C and Gamelin D R 2005 J. Am. Chem. Soc. **127** 15568

[13] Kim D H, Yang J S, Lee K W, Bu S D, Noh T W, Oh S J, Kim Y W, Chung J S, Tanaka H, Lee H Y and Kawai T 2002 Appl. Phys. Lett. **23** 2421

[14] Venkatesan M, Fitzgerald C B and Coey J M D 2004 Nature **430** 630

[15] Hong N H, Sakai J, Poirot N and Brize V 2006 Phys. Rev. B **73** 132404

[16] Yoon S D, Chen Y, Yang A, Goodrich T L, Zuo X, Arena D A, Ziemer K, Vittoria C and Harris V G 2006 J. Phys.: Condens. Matter **18** L355

[17] Pammaraju C D and Sanvito S 2005 Phys. Rev. Lett. **94** 217205

[18] Lu J B, Yang K S, Jin H, Dai Y and Huang B B 2011 J Solid State Chem. **184** 1148

[19] Singhal R K, Kumar S, Kumari P, Xing Y T and Saitovitch E 2011 Appl. Phys. Lett. **98** 092510

[20] Berry A J, Walker A M, Hermann J, O'Neill H St C, Foran G J and Gale J D 2007 Chem. Geol **242** 176

[21] Chen L X, Rajh T, Wang Z Y and Thurnauer M C 1997 J. Phys.Chem. B **101** 10688

[22] Wagemaker M, Lutzenkirchen-Hecht D, Keil P, van Well A.A and Frahmb R 2003 Physica B **336** 118

[23] He J, Behera R K, Finnis M W, Li X, Dickey E C, Phillpot S R and Sinnott S B 2007 Acta Materialia **55** 4325.

[24] Nowotny M K, Bak T, Nowotny J and Sorrell C C 2005 phys. stat. sol. **242** R88

[25] Liu C M, Xiang X, Zhang Y, Jiang Y and Zu X T 2011 CHIN. PHYS. LETT. **28** 127201

[26] Zhou S Q, Čižmár E, Potzger K, Krause M, Talut G, Helm M, Fassbender J, Zvyagin S A, Wosnitza J and Schmidt H 2009 PHYSICAL REVIEW B **79** 113201

[27] Von Oertzen G U and Gerson A R 2007 J. Phys. Chem. Solids **68** 324